INSTRUMENTATION, ARTICLES OF MANUFACTURE, AND ANALYSIS METHODS

CLAIM FOR PRIORITY

This application claims priority to United States provisional patent application Serial Number 60/465,367 filed April 25, 2003, entitled "Mass Spectrometry Instruments and Methods", the entirety of which is hereby incorporated by reference.

TECHNICAL FIELD

The present disclosure relates generally to instrumentation, articles of manufacture, and analysis methods and more particularly to mass spectrometer instrumentation, articles of manufacture comprising digital data, and mass spectrometry methods.

BACKGROUND ART

Analytical instruments and methods are representative of analytical tools that can be used for the identification of unknown samples. Typical analytical instruments and methods can provide at least one level of analysis of a sample.

As an exemplary analytical method, mass spectrometry is perhaps the most widely applicable of all analytical tools available to scientists in the sense that it is capable of providing qualitative and quantitative information about the composition of both inorganic and organic samples. Mass spectrometry can be used to determine the structures of a wide variety of complex molecular species. This analytical technique can also be utilized to determine the structure and composition of solid surfaces as well.

As early as 1920, the behavior of ions in magnetic fields was described for the purposes of determining the isotopic abundances of elements. In the 1960's, a theory describing fragmentation of molecular species was developed for the purpose of identifying structures of complex molecules. In the 1970's, mass spectrometers and new ionization techniques were introduced providing high-speed analysis of complex mixtures and thereby enhancing the capacity for structure determination.

The description provides instrumentation, articles of manufacture, and analysis methods that, in some embodiments, can be utilized to identify unknown samples.

SUMMARY

In one embodiment, analysis methods are provided that include, providing a sample, generating a sample data set using the sample, the sample data set comprising first and second data sets, wherein each of the first and second data sets comprises at

least one of an analytical parameter value and a sample characteristic acquired using the analytical parameter value, wherein the analytical parameter value of the first set is different than the analytical parameter value of the second set; and using the first and the second data sets, identifying the sample.

In one embodiment instruments are provided that include: an ionization source configured to apply different ionization energies to a sample to provide different sample characteristics; and processing circuitry configured to process the different sample characteristics to identify the sample.

BRIEF DESCRIPTION OF THE DRAWINGS

Preferred embodiments of the invention are described below with reference to the following accompanying drawings.

Fig. 1 is a flowchart of an analytical method according to an embodiment.

Fig. 2 is a flowchart of an analytical method according to an embodiment.

Fig. 3a is a functional block diagram of a mass spectrometry instrument according to an embodiment.

Fig. 3b is an illustrative representation of data acquired utilizing the instrument of Fig. 3a. according to an embodiment.

Fig. 4a is a functional block diagram of a mass spectrometry instrument according to an embodiment.

Fig. 4b is an illustrative representation of data acquired utilizing the instrument of Fig. 4a according to an embodiment.

Fig. 5a is a functional block diagram of a mass spectrometry instrument according to an embodiment.

Fig. 5b. are illustrative sample analysis utilizing the instrument of Fig. 5a according to an embodiment.

Fig. 5c is an illustrative representation of data acquired utilizing the instrument of Fig. 5a according to an embodiment.

Fig. 6 is a flowchart of a data processing method according to an embodiment.

Fig. 7 is an illustrative representation of the data processing method of Fig. 6 according to an embodiment.

DESCRIPTION OF THE EMBODIMENTS

At least some embodiments provide analytical instruments including mass spectrometers as well as articles of manufacture and sample analysis methods.

Exemplary configurations of these instruments, articles, and methods are described with reference to Figs. 1-7.

Referring first to Fig. 1, a general flowchart 10 which may be performed by an analytical instrument and having step 12 and step 14 is shown. Step 12 includes multiple parameter sample characteristic acquisition. Typically analytical instruments include one or more analytical components and these analytical components are configured to acquire sample characteristics according to a predefined analytical or acquisition parameter having a value.

Exemplary analytical instruments include mass spectrometry instruments. Exemplary analytical components of mass spectrometry instruments include sample inlet components, analyte modification components, mass separation components, and detection components. An exemplary analytical parameter of the analyte modification component of a mass spectrometry instrument can include ionization energy and ionization energy can have a value. Exemplary sample characteristics acquired using a mass spectrometry instrument include mass spectra of the sample. As will be discussed below, sample characteristics can be acquired utilizing different or multiple acquisition parameter values.

Referring next to Fig. 2 an embodiment of step 12 is shown as sample characteristic acquisition flowchart 20. As exemplified in flowchart 20 sample characteristic acquisition can take place through multiple steps with a first step 22 including providing a sample. For purposes of this disclosure, the sample represents any chemical composition including both inorganic and organic substances in solid, liquid, and/or vapor form. Specific examples of samples suitable for analysis include volatile compounds such as toluene, or other specific examples including highly complex non-volatile protein based structures such as bradykinin. In certain aspects the sample can be a mixture containing more than one substance or in other aspects the sample can be a substantially pure substance. The sample may be of a known composition and as such, referred to as a known or reference sample. Analysis of the sample can be performed according to exemplary aspects described below.

After step 22, step 24 provides for acquiring a first sample characteristic at a first analytical parameter value. Referring to Fig. 3a, an exemplary instrument 40 according to one embodiment is shown that may be utilized in accordance with step 24 of Fig. 2. Instrument 40 may include a sample inlet component 42 configured to receive the sample 44 and convey sample 44 to an analyte modification component 46. Instrument 40 also includes a detection component 48 and processing circuitry 50 that may be coupled to one or more of sample inlet component 42, analyte modification component 46, detection component 48, and/or storage circuitry 52.

Sample 44 can be introduced into sample inlet component 42. Sample inlet component 42 can be configured to introduce an amount of sample 44 into instrument 40 for analysis. Depending upon sample 44, sample inlet component 42 may be configured to prepare sample 44 for introduction into additional analytical components such as analyte modification components and detection components. Types of sample inlets include batch inlets, direct probe inlets, chromatographic inlets, and permeable, semi-permeable, solid phase micro extractions (SPME) and/or capillary membrane inlets. Sample inlet component 42 can also be configured to prepare sample 44 for analysis in the gas, liquid and/or solid phase. Sample inlet component 42 can be configured to provide sample 44 according to sample inlet parameters.

In an exemplary embodiment, sample inlet component 42 can be a chromatographic inlet and the sample inlet parameter of the chromatographic inlet can be a parameter than influences elution of sample 44 or portions of sample 44 from the chromatographic inlet. In one aspect, where the chromatographic inlet is a gas chromatographic inlet, an exemplary sample inlet parameter can include the temperature value of a chromatography column of the gas chromatographic inlet. In some configurations, sample inlet component 42 may be combined with analyte modification component 46. Sample inlet component 42 can be configured to provide sample 44 to instrument 40 according to multiple configurations. For example sample inlet component 42 can be configured as a liquid chromatograph to acquire a first data set in one instance and configured as a gas chromatograph to acquire a second data set in another instance.

Analyte modification component 46 can be configured in exemplary embodiments to receive sample 44 directly or in other exemplary embodiments to receive sample 44 from sample inlet component 42. Analyte modification component 46 can be any component configured to modify an analyte upon exposure of the analyte to the analyte modification component. For example, analyte modification component 46 can be configured as an ionization component to process/ionize sample 44 according to one or more parameters to form ionized analytes. In this configuration, analyte modification component parameters include ionization parameters that can include parameters that affect one or more of the amount of ionization, dissociation, and/or fragmentation of sample 44 when exposed to analyte modification component 46. In an embodiment analyte modification component 46 is configured to provide first and second ionization parameter values. The formation of ionized analytes from sample 44 can include the bombardment of sample 44 with electrons, ions, molecules and/or photons. The formation of ionized analytes within analyte modification component 46 can also be

preformed by thermal or electrical energy according to the ionization parameter and its value.

Analyte modification component 46 may be configured as, for example, an electron ionization component (EI, typically suitable for gas phase ionization), a photo ionization component (PI), a chemical ionization component, collisionally activated dissociation component (CID), electrospray ionization (ESI), and/or Flame Ionization. Other configurations are contemplated including analyte derivitisation components such as chemical derivitisation components for use in combination with gas chromatography and liquid chromatography. Furthermore, embodiments are contemplated that include analyte modification component 46 configured as multiple components such as both an electron impact ionization source and a chemical ionization source. Other contemplated embodiments include acquiring a data set with analyte modification component 46 configured in one configuration and acquiring another data set with analyte modification component in another configuration. For example a data set can be acquired with analyte modification component 46 configured as electron ionization component and another data set can be acquired with analyte modification component 46 configured as chemical ionization component.

In one aspect, when the analyte modification component is configured as an ionization component it can be configured provide an ionization component parameter value. An exemplary ionization component parameter value that may be provided by analyte modification component 46 is the amount of ionization energy provided to sample 44. And upon providing one amount of ionization energy at least one ionized analyte or analytes can be formed and upon providing another amount of ionization energy another analyte or analytes can be formed. In reaction form, this is demonstrated by equation 1 below:

$$M + E \rightarrow M^{+\bullet} + E' \rightarrow M^{+} + F^{+} + N + E'' \quad (1)$$

wherein M represents the neutral analyte, E represents the energy provided to M; $M^{+\bullet}$ represents an internally excited ion; E' represents any E not deposited into $M^{+\bullet}$ as internal or kinetic energy; M^{+}, F^{+} and N represent charged analyte, charged dissociation products, and neutral dissociation products, respectively; and E'' represents any E not remaining in M^{+}, F^{+} or N as internal or kinetic energy. In one embodiment anayte modification component 46 can impact the amount of dissociation of sample into these other molecules (F^{+} and N).

According to one aspect, a first ionization parameter value can include the ionization energy of an electron ionization source, a second ionization parameter value can include the ionization energy of the electron ionization source, and the first ionization energy can be less than the second ionization energy.

In an exemplary embodiment, analyte modification component 46 can be configured as an electron impact ionization component and an analyte modification parameter value of the electron impact ionization component can be the amount of energy provided by the electron impact ionization component. One exemplary impact ionization component parameter value that may be utilized is an electron impact energy of about 10 eV to form an ionized analyte or group of ionized analytes. Another exemplary impact ionization component parameter value that may be utilized is an electron impact energy of ionization of about 70 eV to form another ionized analyte or group of ionized analytes.

In an exemplary embodiment, analyte modification component 46 can be configured as a photo ionization component and an analyte modification parameter value of the photo ionization component can be a parameter that influences the formation of ionized analytes of sample 44. For example, analyte modification parameter value can be a photo energy of the photo ionization component that can be applied at different values to vary the internal energy of the sample and provide ionized analytes having different characteristics.

In another exemplary embodiment, analyte modification component 46 can be configured as an electrospray ionization component and the analyte modification parameter value of the electrospray ionization component can be a parameter that influences the formation of ionized analytes of sample 44. For example, one electrospray ionization component parameter that can be applied at different values and provides differing ionized analytes from the same sample is the pressure value under which the electrospray ionization component processes the sample. Another electrospray ionization component parameter that can be applied at different values and provides differing ionized analytes from the same sample is the potentials applied when transporting ions from the atmospheric pressure into the vacuum of instrument 40 (often referred to as "nozzle/skimmer" or "cone voltage" disassociation).

Analytes modified in analyte modification component 46 can be detected in detection component 48. Exemplary detection components include electron multipliers, Farady cup collectors, photographic, scintillation-type detectors, UV, UV-vis, diode-array, thermal conductivity, atomic adsorption, FID's. In an exemplary embodiment detection of these modified analytes can indicate the characteristics of sample 44 referred to as sample characteristics. In one embodiment, sample characteristics can be acquired and correlated with respective ones of different values of an analytical parameter used to acquire the characteristic (e.g., ionization energy applied to the sample). At least one sample characteristic that can be recorded includes total ion current in one embodiment.

In one embodiment, the progression of mass spectrometry analysis from sample inlet component 42 through analyte modification component 46 to detection component 48 can be controlled and/or monitored by processing circuitry 50 in the described exemplary embodiment. Processing circuitry 50 may be implemented as a processor or other structure configured to execute executable instructions including, for example, software and/or firmware instructions. Other exemplary embodiments of processing circuitry 50 include hardware logic, PGA, FPGA, ASIC, and/or other structures. These examples of processing circuitry 50 are for illustration and other configurations are possible.

Processing circuitry 50 can be configured to control the values of analytical component parameters described above and monitor detection component 48. Control of the analytical component parameter values by processing circuitry 50 can include, for example, dictating a predefined application of ionization energy by analyte modification component 46. In one embodiment, processing circuitry 50 can be configured to control analyte modification component 46. In an exemplary aspect, processing circuitry 50 can dictate a value of an analyte modification parameter during a first moment in time and a different analyte modification parameter during a second moment in time. Exemplary monitoring includes the recording of data received from detection component 48. By varying analytical component parameter values utilized as described sample characteristics can be obtained and associated with the parameter values and provided in the form of respective data sets according to the different values.

In one aspect processing circuitry 50 may execute data acquisition and searching programming and be configured to perform data acquisition and searching that includes the acquisition of sample characteristics such as total ion current or mass spectra. In another aspect, processing circuitry 50 can be configured to associate detected sample characteristics such as total ion current responsive to one or more analytical parameters such as an ionization parameter including electron impact ion source energy. Processing circuitry 50 can be configured to monitor detection component 48 and associate detection of first analytes with a first sample characteristic and detection of second analytes with a second sample characteristic. Processing circuitry 50 may also be configured to associate both the first sample characteristic with the first value of the analytical parameter, and the second sample characteristic with the second value of the analytical parameter. In an exemplary embodiment processing circuitry 50 can be configured to correlate both the first value of analyte modification parameter provided from analyte modification component 46 with the analytes detected during the first moment in time, and the second value of the analyte modification parameter provided from analyte modification component 46 with the analytes detected

during the second moment in time. Processing circuitry 50 can also be configured to prepare a sample data set that may include first and second data sets corresponding to the respective values.

Referring again to Fig. 2, after step 24, step 28 provides for preparing a first data set of the first analytical parameter value associated with the first sample characteristic acquired in step 24 and step 30 provides for preparing a second data set of the second analytical parameter value associated with the second sample characteristic acquired in step 26. Following steps 28 and 30 of flowchart 20, step 32 provides for the preparation of sample data sets of the first and second data sets prepared in steps 28 and 30 respectively. In an exemplary embodiment, sample data sets acquired by analyzing reference samples may be referred to as reference data sets and sample data sets acquired by analyzing unknown samples may be referred to as unknown sample data sets.

Referring to Fig. 3b, an exemplary sample data set 60 is shown that includes a first data set 62 and a second data set 64. Sample data set 60 can include additional data sets as well. First and second data sets 62 and 64 may correspond to different values of an analytical parameter. According to the exemplary embodiment depicted in Fig. 3b, the analytical parameter is the ionization energy of analyte modification component 46 and the sample characteristic is the total ion current detected by detection component 48. As further depicted in Fig. 3b, sample data set 60 includes values of the analytical parameter that are not equal.

Referring again to Fig. 3a, processing circuitry 50 can be configured to store and access data from storage circuitry 52. Storage circuitry 52 is configured to store electronic data and/or programming such as executable instructions (e.g., software and/or firmware), data, or other digital information and may include processor-usable media. Processor-usable media includes any article of manufacture which can contain, store, or maintain programming, data and/or digital information for use by or in connection with an instruction execution system including processing circuitry in the exemplary embodiment. For example, exemplary processor-usable media may include any one of physical media such as electronic, magnetic, optical, electromagnetic, and infrared or semiconductor media. Some more specific examples of processor-usable media include, but are not limited to, a portable magnetic computer diskette, such as a floppy diskette, zip disk, hard drive, random access memory, read only memory, flash memory, cache memory, and/or other configurations capable of storing programming, data, or other digital information.

Storage circuitry 52 may store a plurality of data sets including first and second sets of data. In exemplary embodiments, the first set of data can include a plurality of

sample characteristics obtained by a given value of a parameter as described above. The second set of data can include a plurality of sample characteristic obtained by a different value of the parameter as described above. As described above, these sample characteristics can include mass spectra and the parameter values which may be varied can include one or more of inlet, analyte modification, and/or detection component parameters. In exemplary embodiments these data sets are associated by a sample. According to one aspect, the first and second sample characteristics can be of the same sample and according to an exemplary embodiment, the value of the acquisition parameters of the first set can be different than the value of the acquisition parameters of the second set.

Referring next to Fig. 4a, according to another embodiment, an instrument 70 is shown that includes mass separation component 72 coupled to analyte modification component 46 and detection component 48. Instrument 70 includes processing circuitry 50 that can be coupled to mass separation component 72. As exemplified processing circuitry 50 can be utilized to control mass separation component 72 and in an exemplary embodiment allow ionized analytes of a predetermined mass-to-charge ratio to proceed to detection component 48 for detection.

Mass separation component 72 can include one or more of linear quadrupoles, triple quadrupoles, quadrupole ion traps (PAUL), cylindrical ion traps, linear ion traps, rectal linear ion traps, ion cyclotron resonance, quadrupole ion trap, time-of-flight mass spectrometers, ion mobility or other structures. Mass separation component 72 can also include focusing lens as well as tandem mass separation components such as tandem ion traps or an ion trap and quadrupole ion trap in tandem.

In one implementation at least one of multiple tandem mass separation components can be an ion trap. Tandem mass separation components can be placed in series or parallel. In an exemplary implementation, tandem mass separation components can receive ions from the same analyte modification component 46. In an exemplary aspect the tandem mass separation components may have the same or different geometric parameters. The tandem mass separation components may also receive analyte ions from the same or multiple ionization components.

An exemplary mass separation component 72 useful in accordance with one embodiment is a cylindrical ion trap (CIT). CIT's typically include three components; a trapping volume, and two endcaps. Typically an AC current or RF voltage is applied to the trapping volume at a predefined rate (e.g., controlled by 50) to eject trapped analytes which are subsequently detected. RF voltage ramps may include variables such as power and/or frequency. Combinations of these variables in predefined amounts are typically referred to as waveforms. Generally, waveforms can be optimized to increase

detection of specific analytes of interest. Waveforms can also be optimized to allow for multiple stages of mass analysis.

In an exemplary embodiment, mass separation component 72 can be a cylindrical ion trap and the mass separation parameter of the cylindrical ion trap can be a parameter than influences the mass-to-charge ratio of ionized analytes received by detection component 48. An exemplary cylindrical ion trap parameter value that influences the mass-to-charge ratio of ionized analytes received by detection component 48 is a mass-to-charge ratio range that can be specified as waveform values.

Utilizing mass separation component 72 in conjunction with analyte modification component 46, detection component 48, and processing circuitry 50, sample characteristics of sample 44 may be obtained that can include mass spectra.. Mass spectra is another sample characteristic that can be associated with values of an analytical parameter such as sample inlet component, analyte modification component, and/or detection component parameter values.

Sample data sets acquired using instrument 70 can include mass spectra as a sample characteristic of first and second ionized analytes detected. Processing circuitry 50 can be configured to associate the ionized analytes detected with the different values of the analytical parameters provided by analytical components such as sample inlet component 42 (e.g., chromatography temperatures), analyte modification component 46 (e.g., ionization energies), and separation component 72 (e.g., waveforms). Processing circuitry 50 can also be configured to associate a group of analytes detected with the analytical parameter values utilized by instrument 70. Processing circuitry 50 can also, at a first moment in time, control mass separation component 72 to provide a first mass separation parameter value that may include a specific mass-to-charge ratio or range of ratios of analytes to proceed to mass detection component 48. Processing circuitry 50 may be configured to acquire sample data sets during this first moment in time that can comprise a first data set of sample characteristics that are associated with acquisition parameters that can include one or more of first sample inlet, analyte modification, and mass separation parameters and values of the respective parameters.

Processing circuitry 50 may also control analyte modification component 46 to provide a second ionization parameter value at a second moment in time and control mass separation component 72 to provide a second mass separation parameter value at that second moment in time that can include allowing specific mass-to-charge ratio or range of ratios of analytes to proceed to mass detection component 48. Data received from detection component 48 during the second moment in time by processing circuitry 50 can include a second data set of sample characteristics that are associated with

respective values of acquisition parameters that can include second sample inlet, analyte modification, and mass separation parameters and values of the respective parameters.

Referring to Fig. 4b, an exemplary data set 80 is shown. Data set 80 includes exemplary data acquired using instrument 70. Data set 80 includes first data set 82 and second data set 84. First data set 82, as exemplarily depicted includes the the analyte modification parameter value of 10 eV, the mass separation parameter mass-to-charge ratio range value of 5-100 m/z, and the sample characteristic mass spectra shown. Second data set 84, as exemplarily depicted includes the analyte modification parameter value of 70 eV, the mass separation parameter mass-to-charge ratio range value of 5-100 m/z, and the sample characteristic mass spectra shown. As exemplified by data set 80, the analyte modification parameter values are different in that the ionization energy at 10 eV is lower than the ionization source energy at 70 eV. According to the exemplary embodiment of Fig. 4a, storage circuitry 52 can be configured to store and provide access to data set 80.

Referring next to Fig. 5a, an instrument 90 is shown configured as a mass spectrometer having a mass separation component 92, an analyte modification component 94, and a mass separation component 96 in addition to previously detailed components. The configuration of instrument 90 is sometimes referred to as a MS/MS or a tandem mass separator configuration.

As exemplarily depicted in Fig. 5a, analyte modification component 46 can be configured to receive sample 44 directly or via sample inlet component 42 and provide, in one embodiment, an ionization energy to sample 44 to form a group of ionized analytes. In an exemplary aspect, analyte modification component 46 can be configured to provide a ionization energy to sample 44 to form a first group of ionized analytes. Analyte modification component 46 can also be configured to provide a second ionization energy to sample 44 to form a second group of ionized analytes. Mass separation component 92 can be configured to receive the first and second groups of ionized analytes and provide both a first separation waveform to separate a first mass-to-charge ratio range of the first group of ionized analytes, and provide a second separation waveform to separate a second mass-to-charge ratio range of the second group of ionized analytes. Analyte modification component 94 can be configured to receive the first and second ranges of ionized analytes and provide both a third analyte modification component parameter value to the first and second ranges of ionized analytes to form a third group of ionized analytes, and provide a fourth analyte modification component parameter value to the ranges to form a fourth group of ionized analytes. Mass separation component 96 can be configured to receive the third and fourth groups of ionized analytes and provide both a third separation waveform to separate a third mass-

to-charge ratio range of the third group of ionized analytes and provide a fourth separation waveform to separate a fourth mass-to-charge ratio range of the fourth group of ionized analytes. In an exemplary aspect, at least one of the first and second parameter values of one of the analyte modification component parameter values or the separation component parameter values are not equal.

Detection component 48 can be configured to detect the ionized analytes of the third and fourth ranges received from mass separation component 96. Processing circuitry 50 can be configured to monitor detection component 48 and control the application of analytical parameters described above when utilizing instrument 90. Processing circuitry 50 may also be configured to associate detection of ionized analytes of the third range with a first sample characteristic and associate detection of ionized analytes of the fourth range with a second sample characteristic. According to an exemplary aspect, the first and second sample characteristics can be mass spectra and these mass spectra can be associated with analytical parameters utilized during their generation. For example, processing circuitry 50 can be configured to associate both the first mass spectra with one or more of the first ionization energy, the first mass separation waveform, the third energy and the third mass separation waveform. Processing circuitry 50 can also be configured to associate the second mass spectra with one or more of the second ionization energy, the second mass separation waveform, fourth energy, and the fourth separation waveform.

While embodiments of analytical instruments have been shown and described in Figs. 3a, 4a, and 5a, alternative embodiments are contemplated. For example the instruments and methods described herein can be configured to obtain sample characteristics other than mass spectra, instruments configured to obtain sample characteristics including NMR, IR, atomic adsorption, liquid and gas chromatography, and other analytical characteristics are contemplated. With respect to the various components discussed above other component are contemplated as well. For example ion mobility spectrometry components are contemplated as well as liquid and gas chromatography. Furthermore, various orders of components and types of components are contemplated as well. For example different sample inlet components may be utilized to obtain different sample characteristics and these different sample inlet components can be used in combination with the same or different analyte modification components, and the same or different mass separation and detection components.

Referring to Fig. 5b an exemplary data acquisition 100 is shown that includes exemplary acquisitions 102 and 104. Acquisition 102 includes ionization of sample 44 at a first ionization energy of 10 eV followed by ion trap mass separation and isolation of an exemplary first ionized analyte having a m/z ratio of 6. Acquisition 102 further includes

exposure of the first ionized analytes to collisionally induced dissociation (CID) and the detection of mass spectra 106 representing the sample characteristic of sample 44 as acquired using the parameters of acquisition 102. Acquisition 104 includes ionization of sample 44 at a second ionization energy of 70 eV followed by ion trap mass separation and isolation of an exemplary second ionized analyte having a m/z ratio of 4. Acquisition 104 further includes exposure of the second ionized analyte to CID and the detection of mass spectra 108 representing the sample characteristic of sample 44 as acquired using the parameters of acquisition 102. Mass spectra 106 and 108 can be associated with their respective acquisition parameters utilized, to form a sample data set.

Referring to Fig. 5c, exemplary data set 110 is shown. Data set 110 includes exemplary data acquired using instrument 90. Data set 110 includes a first data set 112 and a second data set 114. First data set 112, as exemplarily depicted, includes a plurality of acquisition parameters that include a first analyte modification parameter value of 10 eV, first mass separation parameters that include a mass-to-charge ratio range of 1-6 m/z and an ion trap isolation m/z of 6, a second analyte modification component that includes a CID, a second mass separation parameter mass-to-charge ratio range of 1-6 m/z, and the sample characteristic mass spectra shown. Second data set 114, as exemplarily depicted, includes a plurality of acquisition parameters that include a first analyte modification parameter value of 70 eV, first mass separation parameters that include a mass-to-charge ratio range of 1-6 m/z and an ion trap isolation m/z of 4, a second analyte modification component that includes a CID, a second mass separation parameter mass-to-charge ratio range of 1-6 m/z, and the sample characteristic mass spectra shown. As exemplified by data set 110, the analytical parameters of analyte modification are different in that the first analyte modification parameter value of 10 eV in set 112 is lower than the first analyte modification parameter value of 70 eV in set 114 and the isolation m/z of first data set 112 is 6 m/z and second data set 114 is 4 m/z. Data sets such as data set 110 can be stored by storage circuitry 52.

Referring again to Fig. 1, exemplary flowchart 10 provides for processing of acquired sample characteristics in step 14. Step 14 can include identify a sample being analyzed. Referring next to Fig. 6, processing circuitry 50 can be configured to process the acquired sample characteristics in accordance with step 14 of Fig. 1 as exemplified by flowchart 120. Step 122 provides for accessing reference sample data sets. Reference sample data sets can include data sets as described herein acquired using known samples.

As described above analysis methods are provided that include providing the sample and generating a sample data set using the sample. According to one aspect,

the data set can include first and second data sets, with each of the first and second data sets including an analytical parameter value and a sample characteristic acquired using the analytical parameter value. In one aspect, the analytical parameter value of the first set is different than the analytical parameter value of the second set. In one embodiment individual ones of sample characteristics of the first set can be associated with respective individual ones of the sample characteristics of the second set. Some aspects provide for individual ones of the sample characteristics to be associated with a plurality of analytical parameter values. These sample characteristics may be associated by a reference sample. Sample data sets of reference samples may be accessed by process circuitry and utilized to identify unknown samples that are analyzed utilizing like acquisitions parameters. Processing circuitry may access a plurality of these data sets in response to detection of a plurality of analytes generated using predefined acquisition parameters such as those described above.

After step 122, process circuitry can be configured to sort reference sample data sets by acquisition parameter. In an exemplary embodiment, the sorting can include aligning data sets having like acquisition parameter values to facilitate sample characteristic comparison. Following step 124, an unknown sample data set of a sample to be identified can be accessed and in step 128 the unknown sample data set can be sorted by acquisition parameter thereby aligning sample data sets having like acquisition parameters.

In an exemplary aspect, upon accessing and sorting the reference sample data and the unknown sample data sets, the sample characteristics of the reference and unknown sample data having like acquisition parameters can be compared in step 130. In an exemplary embodiment, this comparison can include applying an accepted sample characteristic comparison algorithm to both the unknown and reference sample characteristics. Accepted algorithms provide match values as a product of the comparison. For example, U.S. patent no. 6,487,523 to Jarman et al., describes in detail a multi variant calibration and fingerprint matching of mass spectrometry. An exemplary sample characteristic comparison algorithm includes NIST Mass Spectral Search Program which is typically used to compare mass spectra.

Upon completion of step 130, a match value of the reference and sample data sets is calculated in step 132 by accumulating the match values of the plurality of comparisons of the reference sample and sample characteristics acquired utilizing like acquisition parameters. Match values indicating a sufficient match of sample characteristics acquired utilizing one and another analytical component parameter values can be relied upon to identify an unknown sample.

Referring to Fig. 7 exemplary reference sample data and acquired sample data are depicted and can be accessed and compared in accordance with flowchart 120 of Fig. 6. In accordance with exemplary step 122 reference sample data 134 is accessed. Data 134 includes data 136 and data 138. Data 136 and 138 both comprise a sample characteristic (e.g., mass spectra) and an acquisition parameter value (e.g., ionization energy). As depicted, data 136 is sorted above data 138. In accordance with exemplary step 126, acquired sample data 140 is accessed. Data 140 includes data 142 and data 144. Data 142 and 144 both comprise a sample characteristic (e.g., mass spectra) and an acquisition parameter value (e.g., ionization energy). As depicted, data 142 is sorted above data 144.

In accordance with step 130 mass spectra of data 136 is then compared with mass spectra of data 142. Mass spectra of data 138 is then compared with mass spectra of data 144. For each comparison a match value is calculated and the calculated match values are summarized. According to one embodiment summarizing includes taking an average of the match values as depicted in Fig. 7. The summarized match values can be relied upon to identify a sample.